



DTIC

ELECTE

JAN 27 1993

CEL-TR-92-17

# MICELLAR ENHANCED ULTRAFILTRATION FOR RECOVERY AND CONCENTRATION OF TRICHLOROETHYLENE IN GROUNDWATER

B. L. ROBERTS,  
J. F. SCAMEHORN,  
S. D. CHRISTIAN,  
E. E. TUCKER,  
H. UCHIYAMA

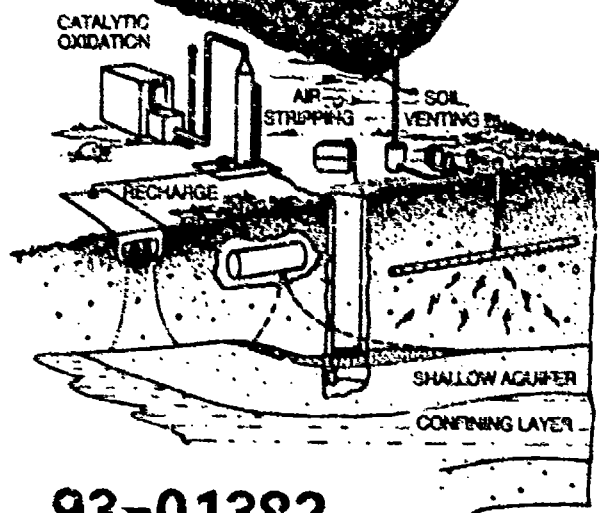
SURFACTANT ASSOC., INC.  
P.O. BOX 2705  
NORMAN, OK 73070

APRIL 1992

FINAL REPORT

JULY 1991 - DECEMBER 1991

APPROVED FOR PUBLIC  
RELEASE: DISTRIBUTION  
UNLIMITED



93-01382



ENVIRONICS DIVISION  
Air Force Civil Engineering Support Agency  
Civil Engineering Laboratory  
Tyndall Air Force Base, Florida 32403



98 1 26 002

NOTICE

PLEASE DO NOT REQUEST COPIES OF THIS REPORT FROM  
HQ AFESC/RD (ENGINEERING AND SERVICES LABORATORY).  
ADDITIONAL COPIES MAY BE PURCHASED FROM:

NATIONAL TECHNICAL INFORMATION SERVICE  
5285 PORT ROYAL ROAD  
SPRINGFIELD, VIRGINIA 22161

FEDERAL GOVERNMENT AGENCIES AND THEIR CONTRACTORS  
REGISTERED WITH DEFENSE TECHNICAL INFORMATION CENTER  
SHOULD DIRECT REQUESTS FOR COPIES OF THIS REPORT TO:

DEFENSE TECHNICAL INFORMATION CENTER  
CAMERON STATION  
ALEXANDRIA, VIRGINIA 22314

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 1992	3. REPORT TYPE AND DATES COVERED Final 1 Jul 91 - 31 Dec 91	
4. TITLE AND SUBTITLE  Micellar Enhanced Ultrafiltration For Recovery And Concentration Of Trichloroethylene In Groundwater			5. FUNDING NUMBERS  F08635-91-C-0917	
6. AUTHOR(S)  Roberts, B.L., Scamehorn, J.F., Christian, S.D., Tucker, E.E., Uchiyama, H.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Surfactant Associates, Inc P.O. Box 2705 Norman, OK 73070			8. PERFORMING ORGANIZATION REPORT NUMBER  Final Report TR-92-17	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  AFCEA/BAVW Tyndall AFB FL 32403-6001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER  CEL-TR-92-17	
11. SUPPLEMENTARY NOTES  Availability Of This Report Is Specified On Reverse Of Front Cover				
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved For Public Release Distribution Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The objective of this experimental investigation was to determine the feasibility of micellar-enhanced ultrafiltration (MEUF) and vacuum stripping process in concentrating and separating trichloroethylene (TCE) from contaminated groundwater. The theory is to add surfactant to the contaminated groundwater to form micelles which bind the TCE molecules. The micelles containing the TCE are then removed by ultrafiltration using a spiral-wound membrane. To remove the TCE from the surfactant, this concentrated solution is vacuum stripped and the surfactant is recycled back to each MEUF stage. Properties such as membrane flux, solubilization equilibrium constant, molecular weight, and Krafft temperature were used to determine the appropriate surfactant. Design calculations were performed to estimate the performance of the vacuum stripper and the approximate number of MEUF units needed to remove 99+ percent of the TCE. Based on these feasibility studies, preliminary cost estimates of applying this technology were calculated to be approximately the same cost as current established technology. Several recommendations for improving and optimizing the performance of this technology were made.				
14. SUBJECT TERMS  Ultrafiltration, Separations, Trichloroethylene, Surfactant, Groundwater			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT  Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE  Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT  Unclassified	20. LIMITATION OF ABSTRACT  UL	

## GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to *stay within the lines* to meet optical scanning requirements.

### Block 1. Agency Use Only (Leave blank).

**Block 2. Report Date.** Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year.

**Block 3. Type of Report and Dates Covered.** State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

**Block 4. Title and Subtitle.** A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

**Block 5. Funding Numbers.** To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract	PR - Project
G - Grant	TA - Task
PE - Program Element	WU - Work Unit Accession No.

**Block 6. Author(s).** Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

**Block 7. Performing Organization Name(s) and Address(es).** Self-explanatory.

**Block 8. Performing Organization Report Number.** Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

**Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es).** Self-explanatory.

**Block 10. Sponsoring/Monitoring Agency Report Number. (If known)**

**Block 11. Supplementary Notes.** Enter information not included elsewhere such as: Prepared in cooperation with ; Trans of ; To be published in... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

**Block 12a. Distribution/Availability Statement.** Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR).

DOD - See DoDD 5230.24, "Distribution Statements on Technical Documents."

DOE - See authorities.

NASA - See Handbook NHB 2200.2.

NTIS - Leave blank.

### Block 12b. Distribution Code.

DOD - Leave blank.

DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports.

NASA - Leave blank.

NTIS - Leave blank.

**Block 13. Abstract.** Include a brief (*Maximum 200 words*) factual summary of the most significant information contained in the report.

**Block 14. Subject Terms.** Keywords or phrases identifying major subjects in the report.

**Block 15. Number of Pages.** Enter the total number of pages.

**Block 16. Price Code.** Enter appropriate price code (*NTIS only*).

**Blocks 17. - 19. Security Classifications.** Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

**Block 20. Limitation of Abstract.** This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

## **EXECUTIVE SUMMARY**

### **A. OBJECTIVE**

This purpose of this project was to examine the feasibility of a new separation process, Micellar-Enhanced Ultrafiltration (MEUF), to remove 99+ percent of trichloroethylene (TCE) from polluted groundwater.

### **B. BACKGROUND**

Trichloroethylene (TCE) has been widely used in degreasing operations and as an industrial solvent. As a result, groundwater and soil under major industrial sites are frequently polluted with TCE. Air Force sites with depot level maintenance facilities often have TCE pollution problems because of the extensive use of this compound as a degreasing and paint stripping agent in airplane maintenance operations.

MEUF involves adding surfactant (detergent) to the polluted groundwater. The surfactant forms aggregates called micelles which bind the TCE. The micelles containing the TCE are removed by ultrafiltration (Figure 1). A wide range of organic compounds have been very successfully removed from aqueous streams in a laboratory setting (Table 1). By the use of several stages, 99+ percent of the TCE can be removed from the water. The economics of the process require that the surfactant be recovered. The TCE-rich surfactant solution is treated by vacuum stripping to separate the TCE from the surfactant, so the latter can be reused. The only effluent from the process is the purified water and a small volume of almost pure TCE (Figure 3 and 4).

### **C. SCOPE**

This project involves the experimental investigation of the MEUF process and the vacuum stripping operation for removing TCE from water. As a result of these investigations for several surfactants, a surfactant of choice is selected and design parameters generated for that system. Design calculations are then performed to estimate the performance of the vacuum stripper and the MEUF units in a variable number of stages in a commercial process. Finally, based on these feasibility studies, preliminary economic estimates of the cost of applying this technology are made.

### **D. METHODOLOGY**

The equilibrium distribution ( $K_d$ ) of TCE between the micellar and water phases was studied by equilibrated liquid-vapor samples to determine the maximum TCE rejection for a given surfactant for the MEUF process. A spiral-wound ultrafiltration system (Figure 2) was used to evaluate the separation of TCE from water by using the MEUF process. A TCE-surfactant solution was sprayed into an evacuated vessel to study the volatilization of TCE from a surfactant solution.

## E. TEST DESCRIPTION

The liquid-vapor equilibrium  $K_s$  studies were accomplished by allowing known solution concentrations of TCE and surfactant in water to isothermally equilibrate with the vapor headspace in the sample vial. The TCE concentration in the vapor headspace was evaluated by gas chromatography with flame ionization detector. The ultrafiltration system was operated with all process streams recycled to a temperature controlled feed tank. A purge-and-trap method in conjunction with gas chromatography and a Hall detector was used to evaluate TCE concentrations from MEUF studies and vacuum stripping experiments. The the vacuum stripping of TCE from a surfactant solution was accomplished by spraying the solution into a 20-liter evacuated glass vessel repeatedly.

## F. RESULTS

The solubilization of TCE in four different surfactants was studied by the liquid-vapor equilibrium method (Figures 7-9). Separation of TCE from water using the MEUF process with DOWFAX 8390 has TCE rejections very similar to predicted rejections calculated from liquid-vapor studies (Table 3). TCE rejections of 85 to 88 percent were observed for a single pass operation and decreases in feed stream temperature reduces permeate flux. TCE was found to be easily volatilized from a surfactant solution (Table 4). The relative permeate flux of four different surfactants using 10,000 MWCO ultrafiltration membranes was studied (Figure 5). Permeate surfactant cost and recovery studies using 500 MWCO were accomplished (Figure 10-12). Of the four surfactants evaluated DOWFAX 8390 has the best overall performance when considering TCE solubility, permeate flux, and surfactant recovery.

The experimental results were used to make engineering calculations and cost estimates to determine cost-effectiveness of this novel separation technology relative to fully developed technologies. The MEUF process in conjunction with vacuum stripping can remove 99+ percent of the TCE from groundwater at \$6.66 per 1000 gallons compared to \$4 to \$6/1000 gallons for fully developed technologies for a 100,000 gallon/day facility.

## G. CONCLUSIONS

The MEUF and vacuum stripping operations were shown to be feasible in laboratory experiments. The MEUF process is an extremely young concept and has substantial potential for improvement and optimization. Studies need to continue with developments to: (1) extend the operating range of concentrations on the retentate side of the membrane, (2) enhance TCE solubility in the micelle, (3) improve permeate flux, and (4) decrease permeate surfactant concentrations. Reduction in the cost/unit of one-half to one-fourth is anticipated. This feasibility study of MEUF shows enough promise to justify further work to improve its performance.

## H. RECOMMENDATIONS

The process needs to be demonstrated with a pilot unit on a site with TCE contaminated water to establish the significance of this novel separation technique.

DTIC QUALITY INSPECTED 5

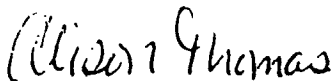
Accession For	
NTIS <del>UNCLASS</del>	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or	
Dist	Special
A-1	

## PREFACE

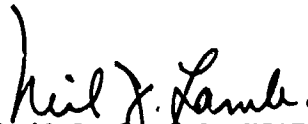
This report was prepared by Surfactant Associates, Inc., P.O. Box 2705, Norman, OK 73070, under Contract Number FO8635-91-C-0197, and sponsored by Air Force Civil Engineering Support Agency (AFCESA/RAVW), Tyndall Air Force Base, Florida 32403-6001. The report was authored by B.L. Roberts, J.F. Scamehorn, S.D. Christian, E.E. Tucker and H. Uchiyama. The AFCESA/RAVW project officers were Ms Alison Thomas and Capt Catherine M. Vogel. This report summarizes work accomplished between 1 July 1991 to 31 December 1991.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public.

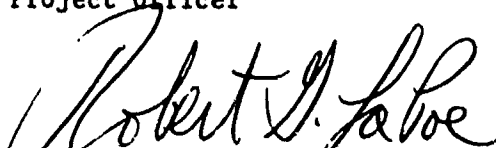
This technical report has been reviewed and is approved for publication.



Alison Thomas  
Project Officer



Neil Lamb, Col, USAF, BSC  
Chief, Environics Division



Robert LaPoe, Maj, USAF, BSC  
Chief, Site Remediation R&D



Frank Gallagher III, Col, USAF, BSC  
Director, Civil Engineering Laboratory



## TABLE OF CONTENTS

Section	Title	Page
I.	INTRODUCTION.....	1
A.	OBJECTIVE.....	1
B.	BACKGROUND .....	1
	1. Basic Principles .....	1
	2. Prior Work.....	3
	3. Process Flow Diagram to Remove TCE from Water.....	4
C.	SCOPE.....	8
II.	RESULTS AND DISCUSSION OF PHASE I WORK .....	9
A.	SEPARATION OF TCE FROM WATER IN MEUF UNITS.....	9
	1. General Considerations .....	9
	2. Flux.....	10
	3. Separation Efficiency.....	14
	4. Spiral-Wound Ultrafiltration Unit Results .....	22
B.	VACUUM STRIPPING.....	22
C.	PROCESS DESIGN CALCULATIONS AND ECONOMICS .....	25
	1. Material Balance Calculations .....	25
	2. Economic Evaluation of Process .....	30
III.	EXPERIMENTAL TECHNIQUES AND APPARATUS ..	34
A.	MICELLAR-ENHANCED ULTRAFILTRATION .....	34
B.	VACUUM STRIPPING.....	35
C.	VAPOR-LIQUID EQUILIBRIUM .....	35
IV.	CONCLUSIONS.....	37
V.	RECOMMENDATIONS .....	38

**TABLE OF CONTENTS  
(CONCLUDED)**

Section	Title	Page
VI. REFERENCES.....		39

## LIST OF FIGURES

Figure	Title	Page
1	Removal of Dissolved Organic from Water Using Micellar-Enhanced Ultrafiltration (MEUF) .....	2
2	Flow Diagram of an Experimental Spiral-Wound Ultrafiltration Apparatus and of a Spiral-Wound Membrane Module. ....	5
3	Process Flow Diagram for Recovery of TCE from Groundwater Using MEUF. ....	6
4	Process Flow Diagram for Recovery of TCE from Groundwater Using MEUF. ....	7
5	The Relative Permeate Flux for Several Surfactants for Spiral Wound and Stirred Cell Studies using 10K MWCO Ultrafiltration Membranes. ....	12
6	Structures of Surfactants .....	13
7	The Solubilization Constant of TCE in 0.05 M DOWFAX 8390 at Different Mole Fractions of TCE in the Micelles ..	15
8	The Solubilization Constant of TCE in 0.05 M Surfactant Solution Composed of 0.9 Mole Fraction DOWFAX 3B2 and 0.1 Mole Fraction STEDBAC at Different Mole Fractions of TCE in the Micelles. ....	16
9	The Solubilization Constant of TCE in 0.05 M CPC Surfactant Solutions at Different Mole Fractions of TCE in the Micelles 20°C and 30°C. ....	17
10	The Cost of DOWFAX 8390 Lost in the Final Permeate Stream .....	19
11	The Permeate Flux for DOWFAX 8390 Using a 500 MWCO Spiral-Wound Ultrafiltration Membrane. ....	20
12	The Permeate Concentration for DOWFAX 8390 using a 500 MWCO Spiral-Wound Ultrafiltration Membrane.....	21

**LIST OF FIGURES  
(CONCLUDED)**

<b>Figure</b>	<b>Title</b>	<b>Page</b>
13	The Effect of the Number of Transfer Units and Stripping Factor on the Reduction Factor for TCE.....	26

## LIST OF TABLES

Table	Title	Page
1	THE REMOVAL OF VARIOUS POLLUTANTS FROM WATER USING MICELLAR-ENHANCED ULTRAFILTRATION.....	3
2	THE EFFECTS OF SOME VARIABLES ON THE VOLUME OF THE RETENTATE STREAM WHICH MUST BE VACUUM-STRIPPED.....	10
3	MEUF DATA FOR TCE USING DOWFAX 8390 AT VARIOUS TEMPERATURES WITH AND WITHOUT ADDED SALTS .....	23
4	RESULTS OF VACUUM STRIPPING OF TCE FROM A 0.2 M DOWFAX 8390 SURFACTANT SOLUTION	27
5	RESULTS OF MATERIAL BALANCE CALCULATIONS ON MEUF PROCESS .....	29

## SECTION I

### INTRODUCTION

#### A. OBJECTIVE

The purpose of this project is to examine the feasibility of a new separation process, micellar enhanced ultrafiltration, to remove 99+ percent of trichloroethylene from polluted water.

#### B. BACKGROUND

Micellar-enhanced ultrafiltration (MEUF) is a novel separation technique which provides the opportunity to remove dissolved organics from wastewater in a process which is potentially much more efficient than alternative methods such as activated carbon adsorption.

In addition to pollution control, there are critical needs for concentration and purification of solutes from water in the production of important industrial materials. A prime example is the concentration of valuable biochemicals from fermentation broth.

##### 1. Basic Principles

A schematic of MEUF illustrating the removal of an organic compound dissolved in water is shown in Figure 1. A surfactant is added to the water at concentrations well above the critical micelle concentration (CMC). Under this condition, most of the surfactant is present as micelles. Micelles are surfactant aggregates containing 50 to 100 molecules for the surfactants to be studied here. The interior of the micelle is a hydrocarbon-like environment. Dissolved organic solutes originally in the water tend to dissolve or "solubilize" in the interior of the micelles.

The solution is then treated by ultrafiltration. The filter membrane pore sizes are small enough to block the micelles and the organic solute associated with these micelles. The concentrations of the organic and surfactant in the permeate (solution passing through the membrane) correspond to their unassociated concentrations in the solution which does not pass through the membrane (the retentate). For a properly designed system, the permeate concentrations of the targeted organics can be very low. The permeate can be discharged to the environment or reused in the plant. The retentate contains almost all of the original solutes in high concentration and is much smaller in volume than the original stream treated. Therefore, MEUF can achieve waste minimization or preconcentration of the targeted organic compounds by concentrating pollutants or products into a stream of relatively small volume in

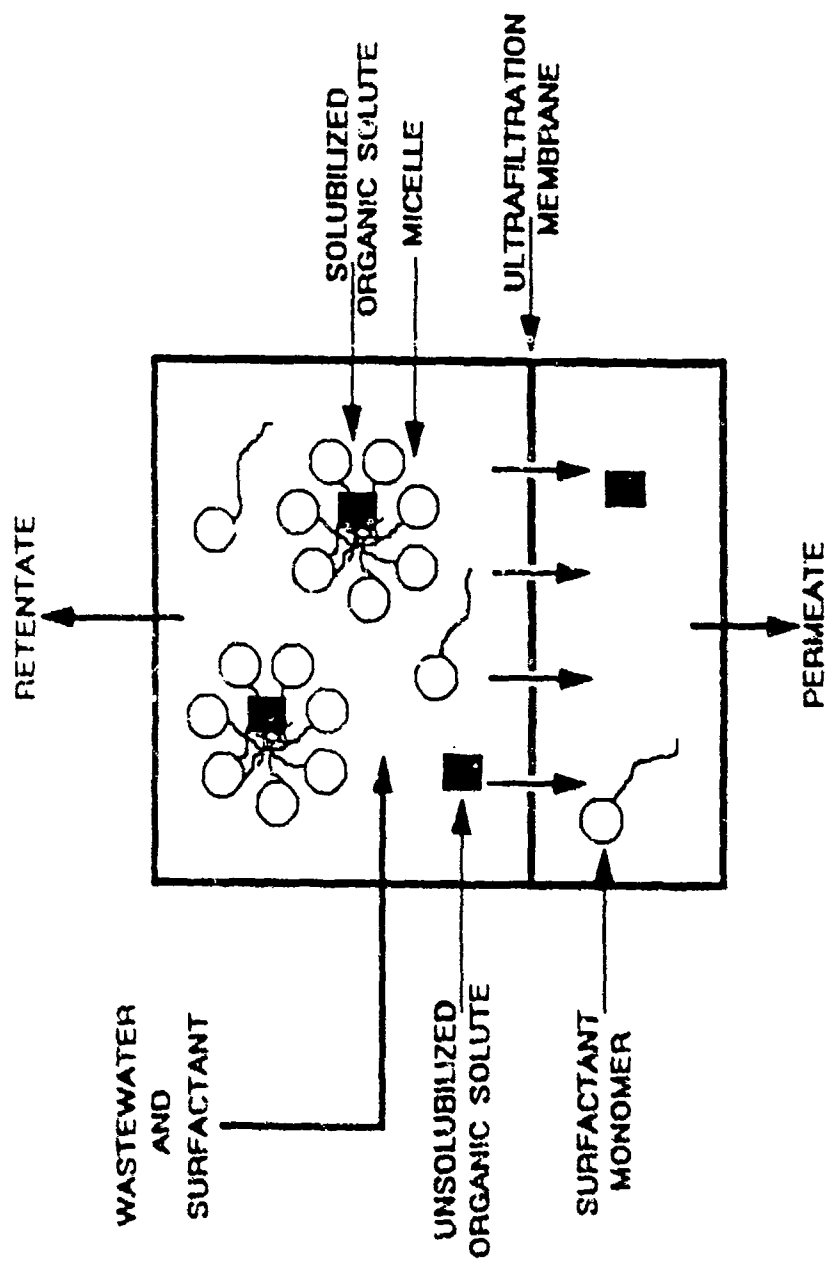


Figure 1: Removal of Dissolved Organic from Water Using Micellar-Enhanced Ultrafiltration (MEUF)

one pass. MEUF may be staged to achieve even purer permeate and/or smaller retentate volumes. The surfactant can be recovered from this retentate solution for reuse.

## 2. Prior Work

The use of micellar-enhanced ultrafiltration for removal of organics from water was first proposed by Leung (2). All subsequent published work on the use of this technique for organic pollutant removal has been published by the senior scientists' research group at the University of Oklahoma (3-13), except for one paper (14).

We have studied the removal of a wide range of organics from water using MEUF. The estimated permeate concentration and rejection of some of these pollutants for a feed stream of arbitrary composition is shown in Table 1.

**Table 1: REMOVAL OF VARIOUS POLLUTANTS FROM WATER USING MEUF.**

<u>POLLUTANT</u>	<u>POLLUTANT CONCENTRATION IN THE PERMEATE</u>	<u>REJECTION</u>
Phenol	1.42 mM	94.3 percent
m-Cresol	0.526 mM	97.9 percent
4-Tert-Butylphenol	0.0767 mM	99.7 percent
Toluene	0.80 mM	96.8 percent
Chlorobenzene	0.49 mM	98.0 percent
n-Octanol	0.141 mM	99.4 percent

Conditions: Retentate [Pollutant] = 25 mM; Retentate [Surfactant] = 250 mM; Pressure = 414 kPa; Membrane - 1K to 20K Molecular Weight Cutoff; Temperature = 30°C

For a target solute, such as t-butylphenol, the concentration of solute in the permeate is less than that in the feed by approximately two orders of magnitude. In general, the less water-soluble the organic solute, the more effectively it is removed. Surfactant Associates Inc. investigators are developing theoretical models to predict the removal efficiency for solutes of arbitrary structure (10,13).



One of the most important characteristics of MEUF is that the percentage of removal of a solute does not decline as the solute becomes more dilute. Since many contaminants are toxic at extremely low concentrations, there is an increasing need for pollution control methods that can cost-effectively reduce pollutant concentrations to ppb levels. MEUF may become a key factor.

Experiments investigating MEUF have used both stirred cell and spiral wound ultrafiltration units. Stirred cells are more convenient in laboratory tests, because they require less solution and less time for a run. Spiral-wound or hollow-fiber units are used in actual industrial practice. A schematic of a spiral-wound ultrafiltration device is shown in Figure 2. The performance of MEUF in removing organic pollutants from water is almost identical (on a unit area of membrane basis) for stirred cell and spiral wound membrane units (15); hence, scale-up of MEUF is straightforward.

### 3. Process Flow Diagram to Remove TCE from Water

The use of MEUF to remove 99+ percent of TCE from contaminated groundwater is anticipated to require multiple stages as will be shown. In each MEUF stage, the retentate will be vacuum-stripped to separate the TCE (as overheads from the stripping column) from the surfactant (removed as bottoms from the stripping column in a concentrated solution). Therefore each stage consists of a MEUF unit and a vacuum stripping column. A four-stage process flow diagram is shown in Figure 3. An alternative configuration is shown in Figure 4, where all the retentates from each of the four MEUF stages are fed to a central vacuum stripper. The concentrated surfactant solution from the stripper is recycled back to each MEUF stage. Either configuration is technically feasible - more detailed studies and economic calculations are necessary to determine the most economical system.

The TCE and water from the stripper overheads are condensed after leaving the vacuum pump discharge. The resultant waste stream will ordinarily be a TCE phase and a water phase saturated with TCE. However, for a very dilute groundwater source stream, the TCE concentration may not be great enough to form a separate phase. In either case, the water phase can be treated by traditional methods such as biological degradation techniques or recycled from the first stage to a stripper. In this latter case, the only effluent will be a very small volume of almost pure TCE. For example, in treating 100,000 gallons of a 1 ppm TCE, the resulting TCE stream would be approximately 1 pound.

Although the surfactant concentration in the ultimate permeate stream from Stage 4 is very low, the cost of the operation can be reduced by treating the permeate to recover the surfactant. We will show data for one method of treating this stream (use of a low MWCO ultrafiltration membrane). Other possible solutions will be studied in a Phase II project, if funded. A small make-up surfactant stream is added to the feed entering Stage 1 to replace the surfactant lost in the permeate from Stage 4. This make-

## SPIRAL WOUND MEMBRANE

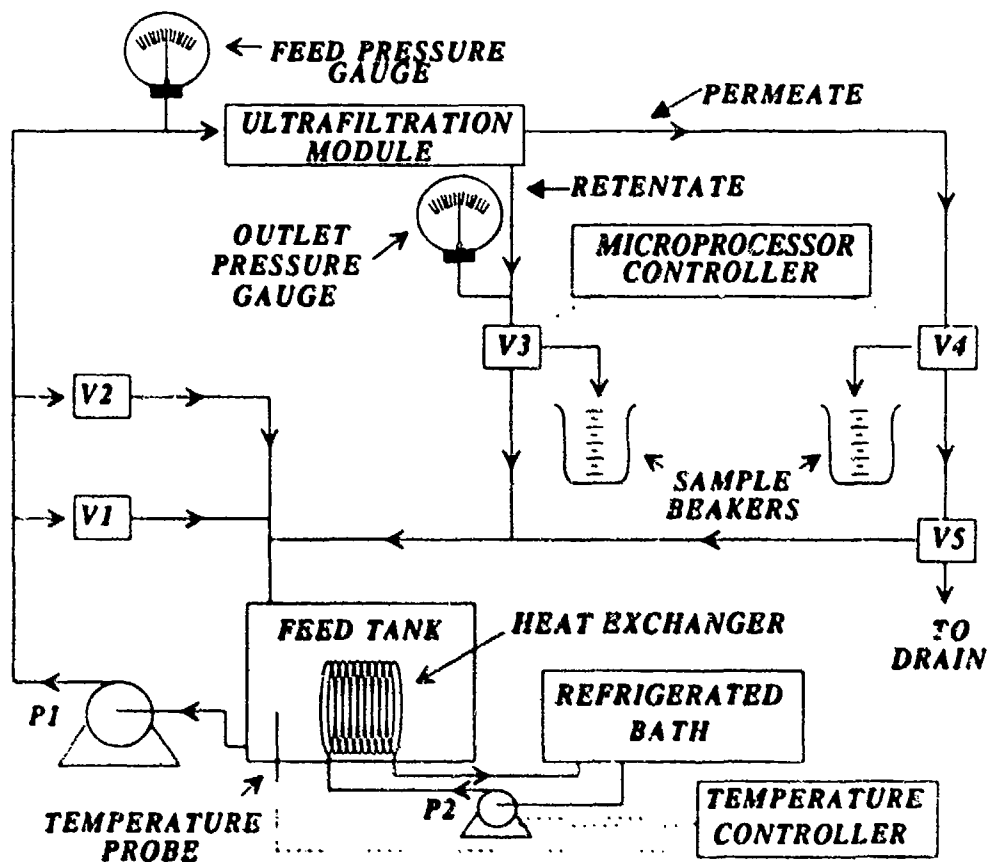
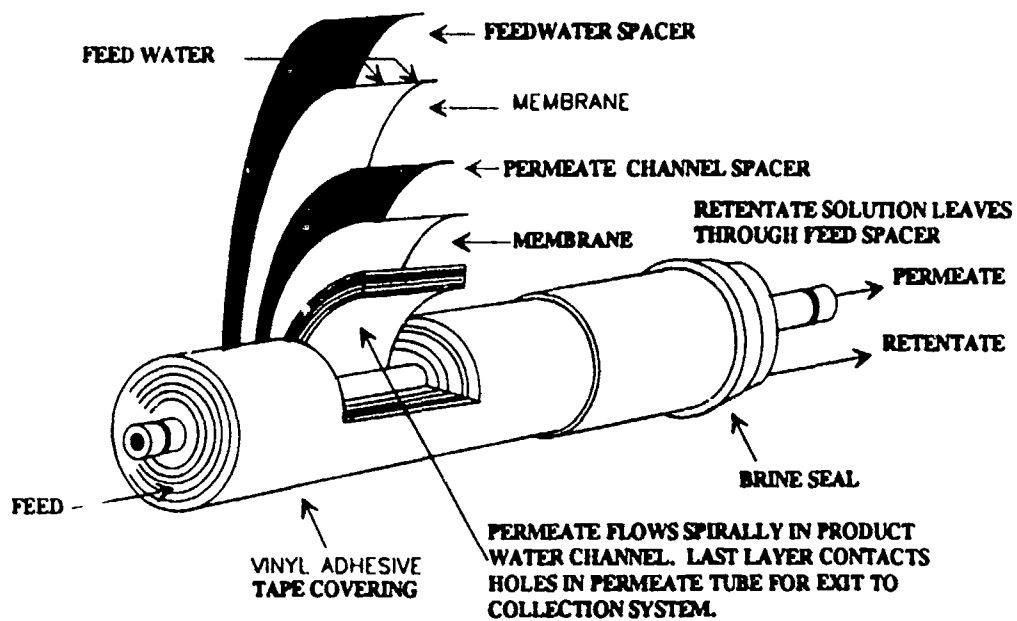


Figure 2: Flow Diagram of an Experimental Spiral-Wound Ultrafiltration Apparatus and of a Spiral-Wound Membrane Module.

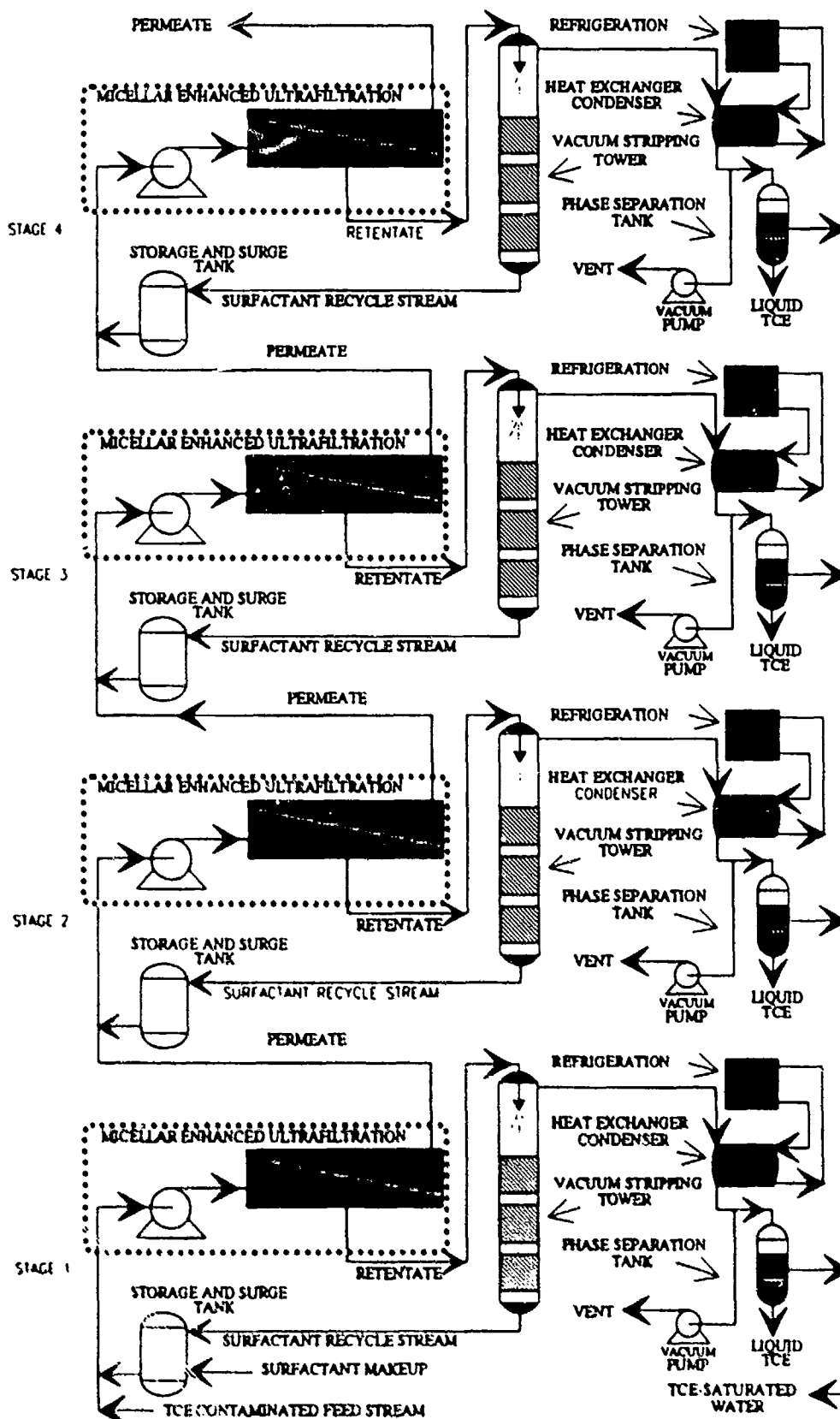


Figure 3: Process Flow Diagram for Recovery of TCE from Groundwater Using MEUF.



up stream could be recovered surfactant from the final permeate, fresh surfactant, or a combination of the two.

The effluent from this process is (1) a water stream containing almost all of the fresh feed water and less than 1 percent of the TCE in the fresh feed, (2) a liquid TCE stream for reuse or disposal - this stream will have a very small volume for the TCE concentrations in the feed of interest here, and (3) potentially a water stream containing a high concentration of TCE, perhaps at saturation. If the stream is recycled to the Stage 1 stripper, this will not be a process effluent; in any case, it will be substantially less than 1 percent of the volume of the fresh feed groundwater.

### C. SCOPE

This project involves the experimental investigation of the MEUF process and the vacuum stripping operation for removing TCE from water. As a result of these investigations for several surfactants, a surfactant of choice is selected and design parameters generated for that system. Design calculations are then performed to estimate the performance of the vacuum stripper and the MEUF units in a variable number of stages in a commercial process. Finally, based on these feasibility studies, preliminary economic estimates of the cost of applying this technology are made.

## SECTION II

### RESULTS AND DISCUSSION OF PHASE I WORK

The results of the Phase I project will be discussed as follows: (1) measurement of the separation efficiency and flux of the MEUF step for each stage; this also includes surfactant recovery from the final permeate stream and selection of the optimum surfactant in this system, (2) measurement and modeling of the stripping step for each stage, (3) process design calculations to optimize the number of stages of the process, the stripping column operation, and to obtain a cost estimate for the process, and (4) a description of the experimental apparatus and techniques used here.

#### A. SEPARATION OF TCE FROM WATER IN MEUF UNITS

##### 1. General Considerations

There are two primary parameters of interest in designing the ultrafiltration units: separation factor (TCE concentration ratio in retentate/permeate), and flux. The number of stages required to attain a separation increases as the separation factor decreases, and the membrane area needed and resulting capital cost increase as the flux decreases. A great deal of work involved selection of a surfactant with acceptable properties.

It has been shown that flux behavior in MEUF follows classical concentration polarization behavior: the flux vs. log (retentate concentration) is linear over a wide range of flux values (4,15,17). For comparison, relative flux is often considered, where relative flux is flux/flux in pure solvent. The pure solvent for this project is water. The ultrafiltration can be performed in a given stage until an unacceptably small flux (generally around a relative flux of 0.1 or 0.2) is attained. This is critical because it dictates the permeate/feed ratio in a given stage. If a substantial increase in the concentration of surfactant and TCE in the retentate cannot be attained in a MEUF stage, the retentate volume which must be stripped becomes quite large and ultimately as much retentate could be stripped as the volume of the original feed stream. One should simply vacuum strip the entire feed stream and not use MEUF. The whole advantage of using MEUF units is to reduce the volume of the streams which must be vacuum stripped to a level well below that of the fresh-feed groundwater stream.

The higher the concentration of surfactant in the feed or the better a surfactant can solubilize the TCE per mole of surfactant, the more solubilization occurs and the lower the TCE concentration in the permeate from that stage - hence, the fewer the number of stages to attain the 99 percent removal of TCE from the water. However, the higher the surfactant concentration to a MEUF stage, the less permeate volume can be produced before the retentate surfactant concentration attains a value too high for

acceptable flux and the higher volume of retentate which must be stripped. Everything else being equal, the more stages in a system, the lower the total retentate stream volume which must be stripped (summed over all stages) since each stage does not have to attain such a high degree of separation for the overall system to attain a 99 percent removal. Hence, we can summarize in Table 2 the effects of some variables on the key variable - the sum of the volumes of the retentate streams which must be vacuum-stripped divided by the volume of the fresh feed. Selection of an appropriate surfactant can cause an increase in the ultimate retentate surfactant concentration (before unacceptably low flux is attained) and can cause an increase in TCE solubilization. Increasing the number of stages adds expense to the process.

**TABLE 2: THE EFFECTS OF SOME VARIABLES ON THE VOLUME OF THE RETENTATE STREAM WHICH MUST BE VACUUM-STRIPPED.**

<b>VARIABLE</b>	<b><u>RETENTATE VOLUME</u> FRESH FEED VOLUME</b>
INCREASING MEUF RETENTATE EFFLUENT SURFACTANT CONCENTRATION	DECREASES
INCREASING SOLUBILIZATION OF TCE IN SURFACTANT	DECREASES
INCREASING NUMBER OF STAGES	DECREASES

## **2. Flux**

In the original proposal, we anticipated using large molecular weight nonionic surfactants since they have extremely low CMC values so that very low surfactant concentration levels in the permeate would be expected (eliminating the necessity of a surfactant recovery from the permeate from the last MEUF stage). Nonionic

surfactants also have the advantage of not precipitating from solution at low temperatures. Figure 5 shows relative flux for DNP-18 (structure given in Figure 6) as a function of retentate surfactant concentration in a spiral wound ultrafiltration unit. At a retentate concentration of about 0.1 M, the relative flux is approximately 0.1. As we will show in staging calculations, this is an unacceptably low flux, so we searched for a different surfactant.

In considering ionic surfactants, we defined several necessary properties: (1) a reasonable flux at high retentate concentrations; (2) a high degree of solubilization of TCE; (3) a low surfactant concentration in the permeate and/or properties which simplify recovery from the permeate from the last stage; and (4) a low Krafft temperature (temperature below which the surfactant precipitates). We selected DOWFAX 8390 (structure shown in Figure 6). The relative flux is shown in Figure 5 for both spiral wound and stirred cell ultrafiltration devices. In a spiral wound device (the type anticipated for commercial use), a retentate concentration of 0.25 M could be attained before the relative flux dropped to 0.1. The DOWFAX 8390 has excellent resistance to precipitation with a Krafft temperature below 0°C. It has a molecular weight of 642 and can be ultrafiltered from the ultimate permeate from the process with a very low MWCO membrane. The solubilization of TCE was also shown to be excellent. Therefore, we have identified DOWFAX 8390 as our surfactant of choice. A Phase II project would involve more effort to improve the surfactant selection and the use of surfactant mixtures, but the performance of DOWFAX 8390 is quite acceptable. Figure 5 also shows the relative flux of DOWFAX 3B2 (structure shown in Figure 6), which is a lower molecular weight version of DOWFAX 8390. This showed a lower flux than the DOWFAX 8390 and was not considered further. A cationic surfactant, stearyl dimethyl benzyl ammonium chloride, was added to DOWFAX 8390 to test the anionic/cationic surfactant mixture. As shown in Figure 5, this system showed a better flux than the anionic surfactant alone, but it was not investigated further because there was concern about the tendency to precipitate at low temperatures. For example, the 10/90 cationic/anionic mole ratio mixture did not appear to precipitate at 30°C, while a 20/80 mixture did precipitate. The limited time available did not allow a complete determination of the precipitation phase boundaries for this system, as would have been necessary. The excellent flux observed in this system makes it a good candidate for study in a Phase II project, because the anionic/cationic surfactant mixture may allow much higher retentate concentrations under certain conditions.

In designing a unit based on the flux data shown in Figure 5, the membrane area per unit flow rate is found by integrating from the inlet feed composition to the effluent retentate composition and finding the total area required - the flux at the beginning of the stage is greater than near the outlet where the retentate concentration is higher.



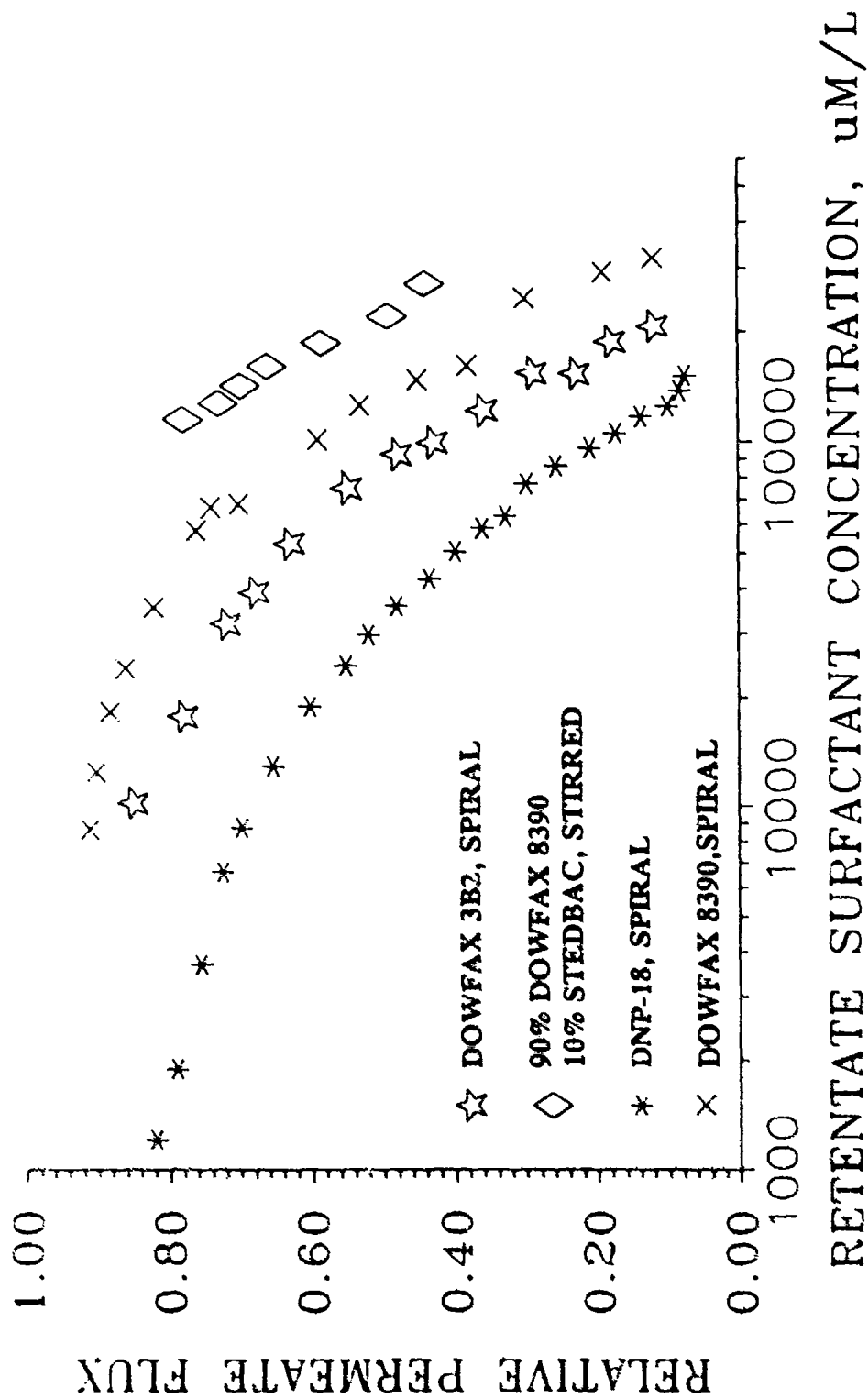
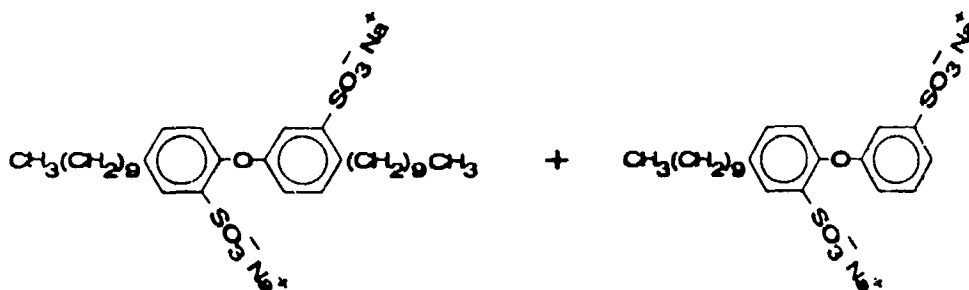


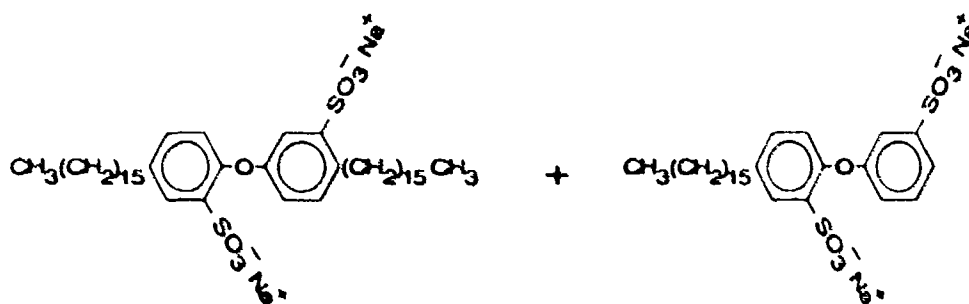
Figure 5: The Relative Permeate Flux for Several Surfactants for Spiral-Wound and Stirred Cell Studies Using 10K MWCO Ultrafiltration Membranes.

**CETYLPYRIDINIUM  
CHLORIDE  
(CPC)**

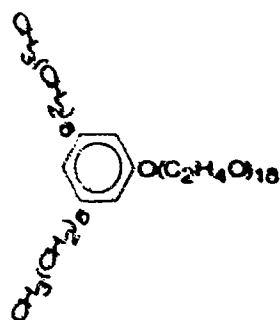
**STEARYL DIMETHYL BENZYL  
AMMONIUM CHLORIDE  
(STEDBAC)**



**DISODIUM DIDECYLDIPHENYLOXIDE + DISODIUM DECYLDIPHENYLOXIDE**  
**DISULFONATE (DOWFAX 3B2) DISULFONATE**



**DISODIUM  
DIHEXADECYLDIPHENYLOXIDE  
DISULFONATE**      **+**      **DISODIUM  
HEXADECYLDIPHENYLOXIDE  
DISULFONATE**  
(DOWFAX 8390)



**POLYOXYETHYLENE (18) DINONYL PHENOL  
(CHEMAX DNP-18)**

### Figure 6: Structures of Surfactants

### 3. Separation Efficiency

In many studies, we have found that the concentration of the organic solute in the permeate is the same as the unsolubilized solute concentration in the retentate (3,4,17). Therefore, equilibrium solubilization data can be used to predict the separation factor or permeate solute concentration in MEUF. Since equilibrium solubilization data are much easier and faster to obtain than actual ultrafiltration data, this fact provides a way to screen surfactants and obtain trends rapidly. Ultrafiltration runs are necessary to confirm this condition for the actual system used and to obtain flux data.

The solubilization equilibrium constant in the limit as  $[TCE] \ll [\text{micellar surfactant}]$  is defined as follows:

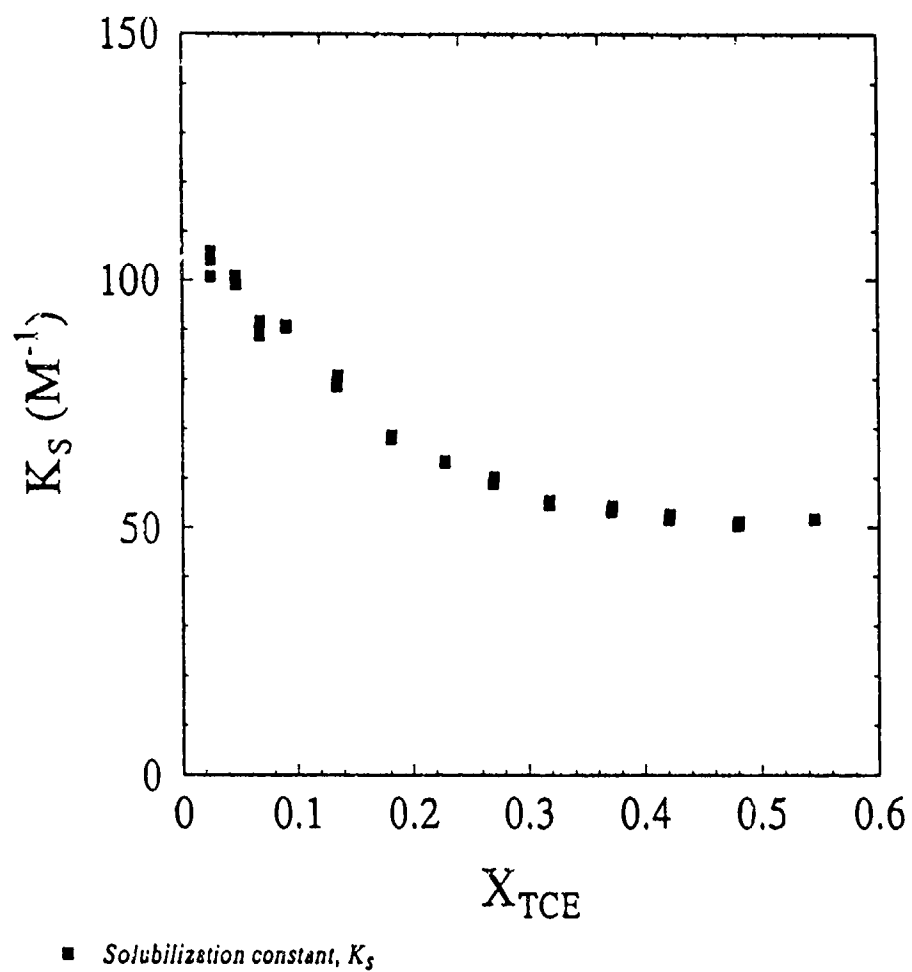
$$K_s = \frac{[\text{solubilized TCE}]}{[\text{unsolubilized TCE}][\text{micellar surfactant}]}$$

where the brackets denote concentrations. Since the unsolubilized TCE concentration is the permeate TCE concentration and the micellar surfactant concentration is the total surfactant concentration in the retentate minus the CMC of the surfactant (which we measure or obtain from the literature), knowledge of  $K_s$  allows prediction of permeate TCE concentration. The value of  $K_s$  for TCE is obtained from head-space chromatography measurements, a traditional technique for measuring solubilization of volatile solutes. (18,19). The higher the value of  $K_s$ , the greater the extent of solubilization and the lower the TCE concentration in the permeate. Later in this report, we will examine the effect of  $K_s$  on the design in a sensitivity analysis in material balance calculations. We will show data confirming that the permeate TCE concentration is equal to the unsolubilized concentration in the retentate for the optimum surfactant found in this study.

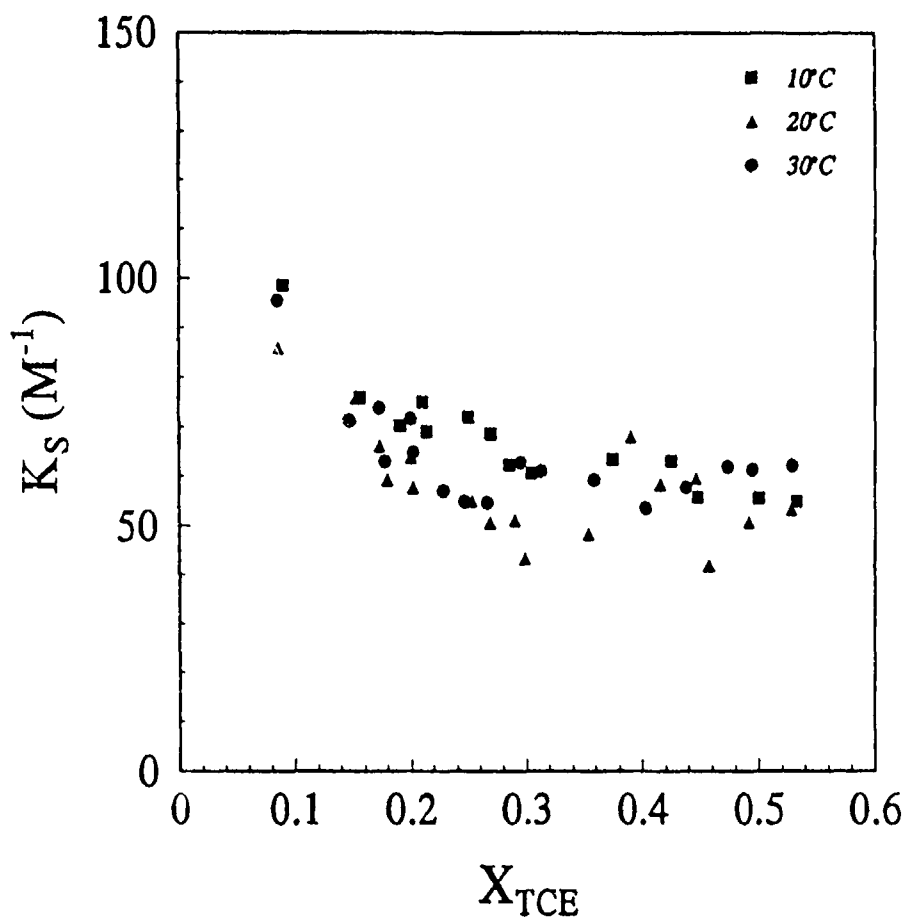
As a part of the search for a good surfactant candidate, undertaken because the flux of the DNP-18 system was found to be unacceptable, we measured  $K_s$  for TCE in a number of surfactant systems as seen in Figures 7-9. The value of  $K_s$  was obtained as a function of mole fraction of TCE in the micelles ( $X_{TCE}$ ).

$$X_{TCE} = [TCE]_{MICELLE} / ([TCE]_{MICELLE} + [SURFACTANT]_{MICELLE})$$

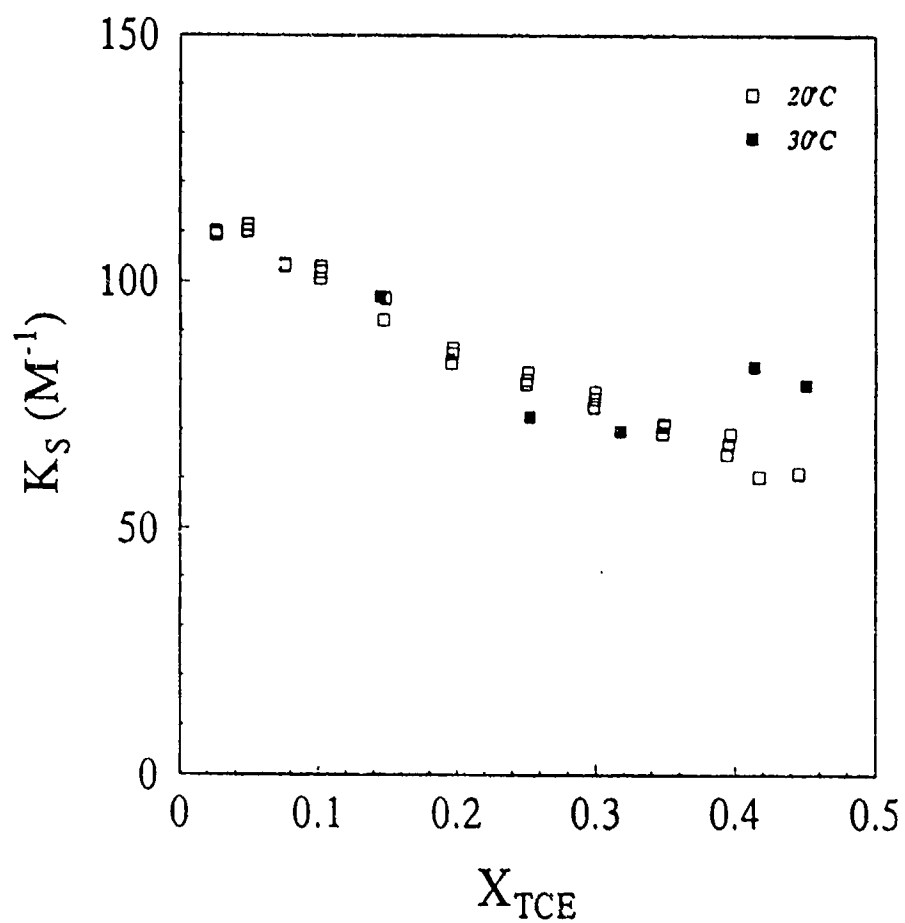
At the very low TCE concentrations in the feed groundwater ( $< 10$  ppm), the  $K_s$  of interest will be essentially at infinite dilution or near  $X_{TCE} = 0$  on the graphs. The data at higher values of  $X_{TCE}$  allow accurate extrapolation to the infinite dilution case.



**Figure 7:** The Solubilization Constant of TCE in 0.05 M DOWFAX 8390 at Different Mole Fractions of TCE in the Micelles.



**Figure 8:** The Solubilization Constant of TCE in a 0.05 M Surfactant Solution Composed of 0.9 Mole Fraction DOWFAX 3B2 and 0.1 Mole Fraction STEDBAC at Different Mole Fractions of TCE in the Micelles.



**Figure 9:** The Solubilization Constant of TCE in a 0.05 M CPC Surfactant Solution at Different Mole Fractions of TCE in the Micelles and at 20°C and 30°C.

The three surfactant systems for which solubilization data are shown in Figures 7-9 are (1) DOWFAX 8390 at 20°C, (2) the cationic surfactant/DOWFAX 3B2 mixture (10/90 mole ratio) at 10°C, 20°C, and 30°C, and (3) cetylpyridinium chloride (CPC) at 20°C and 30°C. All surfactant concentrations are constant at 0.05 M - the value of  $K_s$  is generally independent of surfactant concentration (3,4). The value of  $K_s$  at  $X_{TCE} = 0$  is similar for all these surfactant systems. This is consistent with the solubilization locus being in the interior of the micelle or in the palisade layer (16), so the nature of the hydrophilic group does not have a large effect on solubilization. Also, temperature does not have a significant effect on the solubilization constant, a commonly encountered result in these types of systems (20). These results are significant because they indicate that the separation efficiency is not significantly temperature-dependent. Since groundwater at varying temperatures could be encountered at different times of year or different locales, this makes the system robust with respect to that important variable.

As an example of the significance of the measured value of  $K_s$  at infinite dilution of about  $120 \text{ M}^{-1}$ , consider a retentate with a concentration of 0.25 M DOWFAX 8390. In such a system, the ratio of solubilized to unsolubilized TCE will be 30 or the ratio of TCE in the permeate to that in the retentate will be 1/31. If the retentate-to-feed volume ratio is 1/5, the percentage of TCE removed in this one stage would be 88.6 percent. Of course the material balances in a real system with vacuum strippers and recycle streams are more complex, but this simple calculation indicates the type of separation attainable in one stage. We estimate the optimum number of stages to attain a 99 percent removal of TCE from the feed to be four.

The reluctance to use the cationic/anionic surfactant mixtures because of potential precipitation problems has already been mentioned. The leakage of surfactant into the ultimate permeate stream must be minimal or a downstream surfactant recovery step will be necessary. The permeate concentration of CPC is about 0.8 mM (12,15). The permeate concentration of DOWFAX 8390 was measured during this project to be 0.3 mM. Shown in Figure 10 is the cost per 1000 gallons of treated groundwater for DOWFAX 8390 lost in the final permeate from leakage. The cost of surfactant leakage for CPC is of the same magnitude. Both values are too large to avoid downstream treatment, but the molecular weight of the CPC is 340 while that of the DOWFAX 8390 is 642. As shown in Figures 10 and 11 DOWFAX 8390 could be removed from the permeate from the last stage by ultrafiltration with 500 MWCO membranes (the smallest commercially available), although this would be ineffective for CPC. Figure 11 shows at the anticipated feed concentrations the relative permeate flux is above 0.90 which indicates minimal negative effects on flux due to concentration polarization. Figure 12 shows that 95 percent of the surfactant is rejected (recovered) based on the surfactant feed concentration. The DOWFAX 3B2 for which flux data are shown in Figure 5, also has a molecular weight too low for downstream recovery by ultrafiltration. Therefore, considering flux behavior, solubilization

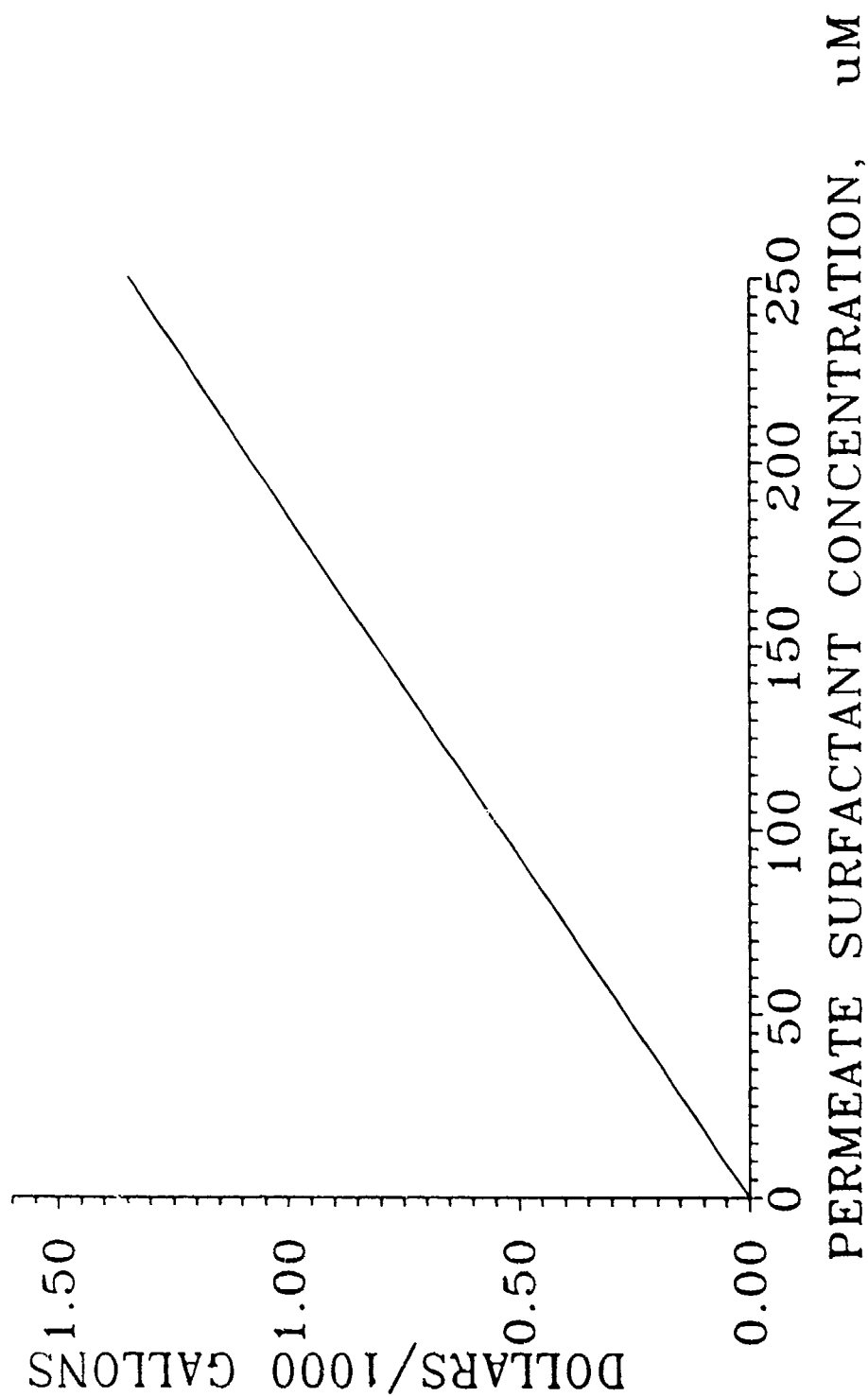


Figure 10: The Cost of DOWFAX 8390 Lost in the Final Permeate Stream.





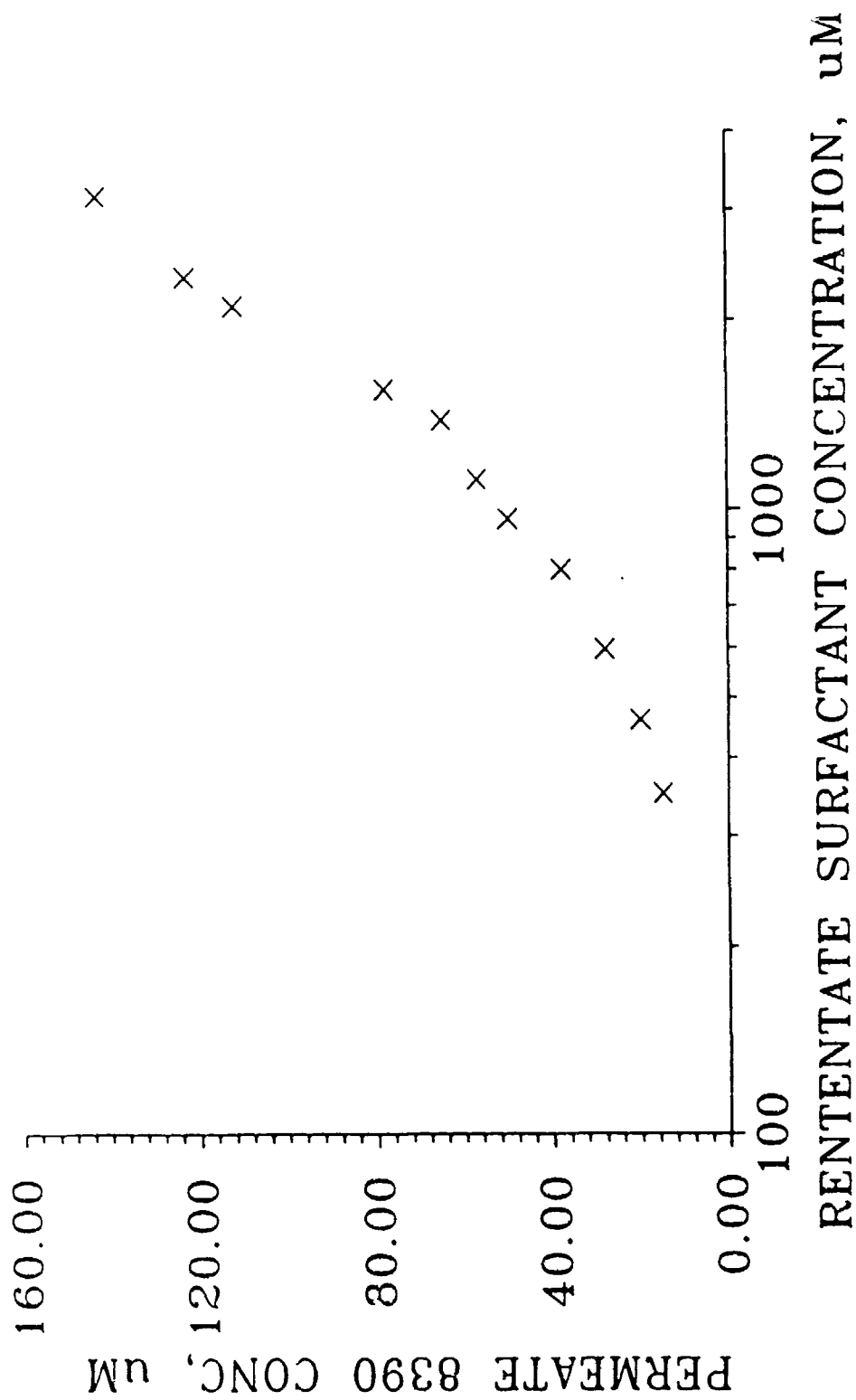


Figure 12: The Permeate Concentration for DOWFAX 8390 Using a 500 MWCO Spiral-Wound Ultrafiltration Membrane.

constant, and downstream permeate concentrations and recovery potential, DOWFAX 8390 qualifies as the best surfactant investigated thus far and all further calculations, designs, and economic estimates in this report will assume use of this surfactant.

#### **4. Spiral-Wound Ultrafiltration Unit Results**

Table 3 shows data from one spiral wound MEUF unit in which flux and TCE rejection were measured at two temperatures (15°C and 30°C) and with added salts expected to be present in the groundwaters encountered (33 percent ferric sulfate, 33 percent ferrous sulfate, and 34 percent calcium sulfate by weight). The retentate flow rate was set at 1.6-liters per minute. The retentate TCE concentration was calculated by using the measured feed TCE concentration, measured permeate TCE concentration, the measured retentate flow rate, and the measured permeate flux and performing a mass balance around the membrane module. There is a TCE concentration gradient on the retentate side of the membrane with the minimum concentration occurring at the inlet of the membrane module and a maximum concentration at the outlet of the module. The average retentate concentration ( feed concentration + retentate concentration /2) is a more informative value than either the feed or retentate concentration. There is no significance attached to the difference between the average retentate TCE concentrations in Table 3 since the feed concentrations varied and permeate fluxes varied from one experiment to the next thus changing the average retentate TCE concentrations. The reason for using percent rejection values is to make valid comparisons between experiments having different: (1) feed concentrations, (2) permeate fluxes, (3) feed temperatures, etc., as well as comparisons between totally different experimental methods. The flux values measured are consistent with those shown in Figure 5. The temperature does not affect the rejection significantly, as predicted by the equilibrium  $K_s$  data, but increased temperature does cause an increase in flux. The predicted permeate TCE rejections from the measured  $K_s$  data are also shown in Table 3. The predictions agree with the measurements well, confirming that the system is nearly at equilibrium as expected from previous systems studied in our laboratory. The presence of the added salts did not affect the ultrafiltration, as expected, since ultrafiltration is not sensitive to such additives as would be reverse osmosis as an example. The flux data in Figure 5 and Table 3, along with the solubilization constant in Figure 6 (confirmed in Table 3) permit a design of the MEUF stages including the vacuum stripping operation.

#### **B. VACUUM STRIPPING**

A major goal of research performed during the Phase I project has been to obtain fundamental data that can be used to determine parameters needed in operating both the MEUF stages and the vacuum stripper used to remove TCE from the concentrated retentate solution. Both the equilibrium solubilization results and initial studies of the

**Table 3: MEUF DATA FOR TCE USING DOWFAX 8390 AT VARIOUS TEMPERATURES WITH ADDED SALTS**

TEMPERATURE (centigrade)	[ADDED SALT] (ppm)	FLUX (g/min)	AVERAGE RETENTATE [TCE] (ppb)	PERMEATE [TCE] (ppb)	PERCENT REJECTION	PREDICTED PERCENT REJECTION
30	0	342	860	99	88	86
30	100	337	645	91	86	86
15	0	255	835	126	85	86
15	100	254	745	104	86	86

removal of TCE in a vacuum column provide the physical data required to define the operating conditions for the vacuum-stripping and the UF separation processes.

For purposes of estimating the performance of the vacuum stripper, we assume that the surfactant concentration in the retentate solution from each of the MEUF stages will be approximately 0.25 M (ca. 160,000 ppm or 1.3 pound per gallon). From Figure 5, for DOWFAX 8390, the surfactant upon which our design calculations are based, this is the concentration where the flux becomes unacceptably low, so it represents the MEUF retentate product/stripper feed surfactant concentration. Based on an assumed feed groundwater TCE concentration of 1 ppm, material balance calculations show that the concentration of TCE in the retentate solutions will vary from about 5 ppm in the first UF stage to approximately 50 ppb in the final stage. However, most of the TCE in the retentate will be bound to the surfactant under these circumstances, and in fact the apparent volatility of TCE from the aqueous solution (determined by the Henry's law constant) will be only approximately 3 percent as great as if the surfactant were not present. This change in apparent volatility or Henry's law constant can be calculated directly from the value of the solubilization equilibrium constant for a given surfactant and the known Henry's law constant for the chlorocarbon in pure water. Thus if the concentration of TCE bound to surfactant micelles is 30 times that of the monomeric TCE, the volatility of TCE from the surfactant solution will be only 1/31 as great as if no surfactant were present.

In designing the vacuum-stripper, the value of the stripping factor (S) will determine how many stages will be required to attain a given percentage removal of TCE. This factor will indirectly dictate the size and number of transfer units needed. The stripping factor is defined by:

$$S = (V/L)y/x$$

where y and x are the respective vapor phase and liquid phase mole fractions of TCE and where V and L are the molar flow rates of vapor and liquid through the stripping column. Under the dilute solution conditions prevailing for the TCE, it can be shown that the percentage reduction in concentration of TCE from each liquid-phase transfer unit to the next is practically constant when multiple transfer units are used. This implies that the required number of overall transfer units ( $N_{tr}$ ), the total fractional reduction in TCE concentration (the reduction factor,  $R_F$ ), and the fractional decrease in TCE concentration from one transfer unit to the next ( $f_R$ ) are simply interrelated by:

$$f_R = 1/S = R_F/N_{tr}$$

Under the operating conditions of the vacuum-stripper, S can be chosen to have a value of 4 if the V/L ratio is maintained at approximately 1/150, so that each transfer unit will reduce the concentration of TCE by a factor of four (that is,  $f_R = 0.25$ ); and the use of three stripping stages ( $N_{tr} = 3$ ) will lead to an overall reduction in TCE

concentration of  $1/64$  (i.e.,  $R_F = .0156$ ). The ratio  $V/L$  will vary inversely with the value of  $S$ . For example, if  $S = 2$ ,  $V/L = 1/75$ ; if  $S = 4$ ,  $V/L = 1/150$ ; and if  $S = 6$ ,  $V/L = 1/225$  for the conditions assumed in operating the vacuum stripper.

The major factor determining the efficiency of stripping is the value of the dimensionless parameter  $m = y/x$ , which is determined by the Henry's law constant for TCE dissolved in pure water and the value of  $K_S$ . At temperatures around  $20^\circ\text{C}$ ,  $y/x$  is approximately  $1.8 \times 10^4$  and the solubilization equilibrium constant is  $K_S = 120 \text{ M}^{-1}$ , so that the  $y/x$  value is reduced to approximately 600 at a surfactant concentration of  $0.25 \text{ M}$ . Consequently,  $S$  can be held at the reasonable value of 4 by using a vapor to liquid molar ratio of  $V/L = 1/150$ . The value of  $y/x$  does not vary by more than 10 percent in the temperature range  $15$  to  $25^\circ\text{C}$ .

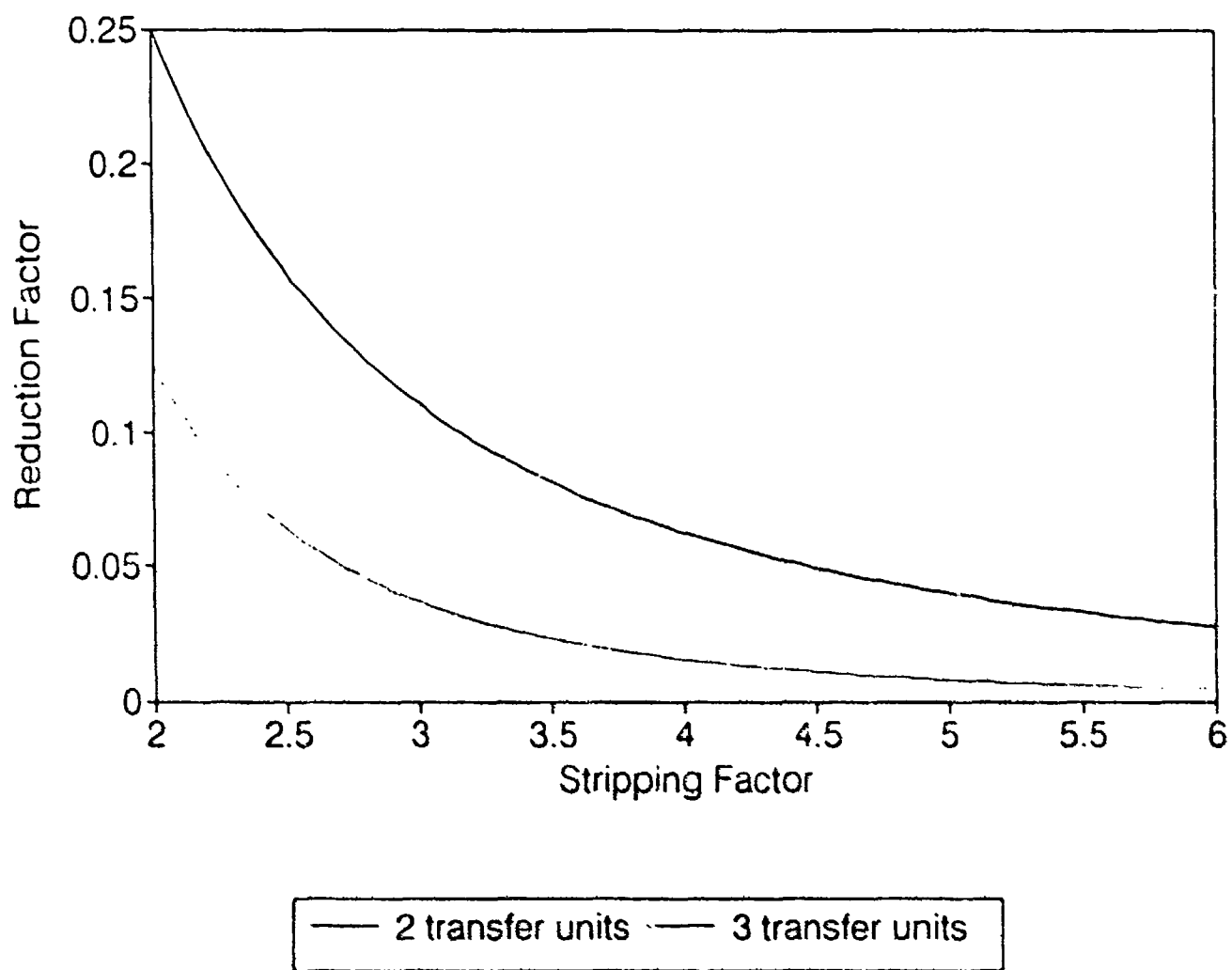
Figure 13 shows the relation between  $R_F$  (the factor by which the TCE concentration is reduced in the stripper) and  $S$ , for an assumed number of transfer units ( $N_{\text{tr}}$ ) equal to two or three) in the stripper. Optimization calculations, have shown that a value of  $R_F$  less than  $0.10$  will be desirable to prevent an excessive amount of TCE from being returned to the process stream in the  $\sim 0.25 \text{ M}$  surfactant solution.

Experiments were performed to test the vacuum stripping of TCE from a concentrated DOWFAX 8390 solution. The results are shown in Table 4 for a single-stage vacuum stripper. The sample was sequentially stripped in this unit and an average of 28 percent removal of TCE was observed.

## C. PROCESS DESIGN CALCULATIONS AND ECONOMICS

### 1. Material Balance Calculations

Material balance calculations were performed on systems of the type shown in Figure 3 (this figure is for four stages) to investigate the performance of this process, but the number of stages was not limited to four. It is assumed that 99 percent of the TCE in the feed is removed. Since the TCE in this stream is so dilute as to be in the Henry's law region, the actual concentration of the TCE is not important: i.e., removal of 99 percent of a  $1 \text{ ppm}$  feed requires the same design parameters as removal of 99 percent of a  $100 \text{ ppb}$  stream. One key parameter indicates the success of the separation: the volume of the retentate streams (sum of retentate streams from each stage) which must be vacuum-stripped. If the volume of this combined retentate stream is equal to that of the feed stream, then the feed stream should be directly vacuum-stripped and MEUF is not worthwhile. On the other hand, if the size of the retentate streams to be stripped is one-third of the size of the feed stream, this can reduce the load on the



**Figure 13: The Effect of the Number of Transfer Units and Stripping Factor on the Reduction Factor for TCE.**

**Table 4: RESULTS OF VACUUM STRIPPING OF TCE FROM A DOWFAX 8390 SURFACTANT SOLUTION**

# OF TIMES STRIPPED	CONCENTRATION PPM TCE	PERCENT REMOVED
FEED	13.9	
1	8.4	40
2	6.5	22.6
3	5.7	12.3
4	4.3	24
5	3.1	28
6	2.2	29
7	1.3	40
8	0.93	28



stripper enough to more than justify the expense of the MEUF units and result in a more economical overall process.

Table 5 shows the results of the material balance calculations. The following variables were investigated: number of stages, surfactant concentration in the retentate, percentage of TCE in the retentate removed per pass in each stage's vacuum stripper (assumed to be the same for each stage), and solubilization constant. In addition to indicating the potential effectiveness of this process, these calculations indicate parameters whose improvement could most enhance the process performance. This provides an indication of the direction future research should take for process optimization.

The base case involves four stages, a retentate surfactant concentration of 0.25, a  $K_s$  of  $120 \text{ M}^{-1}$ , and an assumed 90 percent TCE removed from each retentate stream in the vacuum stripper. The retentate streams from the four stages totaled 30.9 percent of the volume of the feed groundwater. If two stages are used, the volume percent is 64.6 percent; if three stages are used, it is 39.2 percent; if five stages are used, it is 27.2 percent. Hence the number of stages is important, but the advantages of adding stages beyond four diminish rapidly. Hence, four stages are chosen as a base case.

If the retentate surfactant concentration is increased to 0.3 M by selection of a superior surfactant or surfactant mixture, this volume percent decreases from 30.9 percent to 26.0 percent. This potential improvement is one of the reasons for the emphasis on surfactant selection investigation of a Phase II project.

If the value of  $K_s$  increases to  $150 \text{ M}^{-1}$  from  $120^{-1}$ , the volume percent of retentate compared to feed decreases from 30.9 percent to 25 percent, indicating the promise of increasing solubilization capacity for process improvement.

If the percentage of TCE assumed to be removed from each retentate stream in the vacuum stripper is increased from 90 percent to 99 percent, the volume percent of retentate compared to feed decreases from 30.9 percent to 28.2 percent, indicating the relative modest improvements to be gained by stripping the retentate harder.

Finally, if the retentate surfactant concentration is increased to 0.3 M and the value of  $K_s$  increases to  $150 \text{ M}^{-1}$  and if the percentage of TCE assumed to be removed from each retentate stream in the vacuum stripper is increased to 99 percent, the volume percent of retentate compared to the feed decreases from 30.9 percent to 19.0 percent, indicating the substantial improvements possible by reasonable possible improvements in the process.

Table 5: RESULTS OF MATERIAL BALANCE CALCULATIONS ON THE MEUF PROCESS FOR  
TRICHLOROETHYLENE

Number of Stages	4	2	3	5	4	4	4	4
Retentate Surfactant Concentration (M)	0.25	0.25	0.25	0.25	0.30	0.25	0.25	0.30
$K_S$ (M <sup>-1</sup> )	120	120	120	120	120	150	120	150
TCE Removed from Retentate in Each Stripping Column (percent)	90	90	90	90	90	90	99	99
Sum of All Retentate Streams/Feed Streams (Volume/Volume)	0.309	0.646	0.392	0.272	0.260	0.250	0.282	0.190

## 2. Economic Evaluation of Process

The economics presented in this section are based on processing 100,000 gallons per day of TCE contaminated ground water. Capital and operating Costs are based on vendor quotes and general cost correlations from standard sources such as Counce et al (21) and Peters and Timmerhaus (22). The equipment cost was divided into five major categories:

### 1. MEUF Ultrafiltration Units (operated at 50°F)

14 units at \$35,474	\$ 496,640
191 membranes @ \$1100	\$ 210,470

### 2. Vacuum Stripper Column

Stage 1	\$ 25,000
Stage 2	\$ 25,000
Stage 3	\$ 25,000
Stage 4	\$ 25,000

### 3. Vacuum Pump

Stage 1	\$ 7,000
Stage 2	\$ 7,000
Stage 3	\$ 7,000
Stage 4	\$ 7,000

### 4. Condense

Stage 1	\$ 5,000
Stage 2	\$ 5,000
Stage 3	\$ 5,000
Stage 4	\$ 5,000

### 5. Refrigeration

\$ 15,000

### 6. Miscellaneous Tanks, Pumps, and Prefiltration

\$ 50,000

Total Purchased equipment: \$971,110

Total Fixed-Capital Investment was calculated by:

#### Direct Costs

Purchased Equipment	59 Percent
Purchased-Equipment Installation	6
Instrumentation and Controls (installed)	2

Piping (installed)	3
Electrical (installed)	2
Buildings (including services)	3
Yard Improvements	2
Service Facilities (installed)	8
Indirect Costs	
Engineering and Supervision	4
Construction Expense	4
Contractors Fees	2
Contingency	<u>5 Percent</u>
Total Fixed Capital Investment	\$1,645,900

Operating Expenses:

Major Energy Costs:

MEUF

14 units @ 4.2 hp per unit 44 kwh

Vacuum Pump

1 unit @ 10 hp per unit 7.4 kwh

Refrigeration

1 unit @  $7.3 \times 10^4$  BTU/h 21.4 kwh

Total 72.55 kwh

Assuming \$0.07 per kwh the annual cost of electricity is: \$ 43,827

Other Operating Expenses:

Annual cost of membrane replacement: \$ 60,134  
(assumes 3.5 year membrane  
life (\$ 210,470/3.5))

Annual cost of lost surfactant: \$ 2,000  
(assumes permeate concentration  
of 5 micromoles per liter)

Depreciation of Capital Investment: \$ 82,295  
(based on 20 year plant life)

Annual Personnel costs: \$ 50,000

Miscellaneous: \$ 5,000  
(valves, pressure gauges, etc)

The above values are for a plant processing 36,500,000 gallons annually, at a cost of \$6.66 per 1000 gallons of processed groundwater (in 1992 dollars). At the flow rate of 100,000 gallon/day, the economies of scale are not fully realized. Using air stripping with appropriate pollution control devices results in approximately \$4 to \$6/1000 gallons (21). Therefore, this preliminary economic estimate for this process based on only a feasibility study shows that it can result in approximately the same cost for treatment of groundwater as this established technique.

In order to understand how costs may be reduced significantly some knowledge of the membrane configuration is necessary. There are four different membranes used in the TCE recovery system:

- a. 50,000 MWCO membrane (Stage 1)
- b. 50,000 MWCO high flux membrane (Stages 2 & 3)
- c. 10,000 MWCO membrane (Stage 4)
- d. 500 MWCO membrane (surfactant recovery)

The first three stages use 50,000 MWCO membranes but the high flux 50,000 MWCO membranes used in Stage 2 and Stage 3 have twice the flux per unit area compared to the 50,000 MWCO membranes used in Stage 1. The high flux membranes are very susceptible to fouling by particles and are therefore used after the Stage 1 standard 50,000 MWCO membranes which are not as susceptible to fouling and provide permeate, free of harmful fouling particulates, to the follow-on stages. Stage 4 uses 10,000 MWCO membranes which are capable of significantly reducing the surfactant concentration in the permeate stream when compared to a 50,000 MWCO membrane. However, the flux for a 10,000 MWCO membrane is one-half that of a 50,000 MWCO membrane in Stage 1. There is one more stage of membranes not associated with the MEUF process but used for the recovery of surfactant from the Stage 4 permeate stream. The surfactant recovery step uses 500 MWCO membranes with a relative flux approaching that of the 10,000 MWCO membrane mainly because the 500 MWCO membranes are operated within a surfactant retentate concentration range below where concentration polarization unfavorably impacts the permeate flux. The majority of the membranes, almost 70 percent, are located in Stage 4 and the surfactant recovery stage. The minimization of the permeate surfactant concentration is the principal reason for such a high percentage of membranes used in Stage 4 and the surfactant recovery stage. A more effective colloid system may negate the requirement of smaller MWCO membranes thus reducing the cost of the MEUF portion of the plant by almost 63 percent.

The choice of a colloid system that extends the operating range to higher retentate surfactant concentrations may significantly reduce the size of the retentate stream requiring stripping thus reducing the vacuum stripping portion of the plant. A retentate surfactant concentration increase from 0.25 M to 0.50 M will decrease the total

retentate volume requiring stripping by 50 percent and thus reduce the cost of the stripping portion of the plant.

The selection of a colloid system that solubilizes TCE to a greater extent would have the effect of extending the operating range of the surfactant feed concentration to lower concentrations. Lowering the surfactant feed concentration from 0.010 M to 0.005M will decrease the retentate volume by 50 percent. A higher  $K_s$  would also decrease the number of MEUF stages required thus reducing costs associated with both the MEUF and stripper portions of the plant.

This is the first major attempt to evaluate a very young technology for application to concentrate a specific compound on a commercial/industrial scale. The process has tremendous potential if developments are made in the following areas:

- a. The operating range of the surfactant retentate concentration needs to be broadened to reduce the size of the retentate volume requiring regeneration.
- b. Reduce the permeate surfactant concentration or improve the recovery of the surfactant in the final permeate stream on a more cost-effective basis.
- c. A significant increase of solubility of the target organic in the micelle, an increase in the distribution constant ( $K_d$ ), will reduce the number of MEUF stages and reduce the retentate volume requiring stripping.

The MEUF process has substantial potential for improvement and optimization (reasonably, a factor of 2 to 4 improvement in the cost/unit volume might be expected). Therefore, MEUF shows considerable promise as an improved technology for this application.

## SECTION III

### EXPERIMENTAL TECHNIQUES AND APPARATUS

#### A. MICELLAR-ENHANCED ULTRAFILTRATION

A flow diagram of the ultrafiltration apparatus used for this study is shown in Figure 2. The membrane was a 5-Ft<sup>2</sup> square foot cellulose acetate spiral wound membrane manufactured by Spectrum Medical Products. The pump was a Burks stainless steel booster pump, powered by a 1/4 horsepower Franklin 120-volt motor. The temperature of the feed tank was held constant at 15°C or 30°C by pumping refrigerated coolant through a heat exchanger in the feed tank. A temperature probe and controller were used to control the coolant pump to provide the desired temperature in the feed tank. The feed pressure to the membrane was held constant at 60 psi. The retentate flow rate was held constant at 400 milliliters per minute. The apparatus start-up was done with the coarse adjustment pressure control valve (a ball valve) completely open. The feed pressure to the membrane was then set to 60 psi. The retentate and permeate flowrate were measured by actuating two electromagnetic three way valves that diverted the retentate and permeate streams into collection beakers. The beakers, with their solutions, were weighed on a Ohaus triple beam balance and the weight of the empty beakers were subtracted to arrive at mass flow rates for the two streams. The electromagnetic sampling valves were controlled by a microprocessor controller that energize the valves for 15 seconds. Using an iterative process of adjusting the retentate flow rate valve and the fine adjustment pressure control valve and measuring the mass flow rate of the retentate stream the 60 psi feed pressure and 400 milliliter retentate flow rate were established. The three-way system drain valve was used to drain permeate from the apparatus to increase the concentration of surfactant in the feed tank.

The surfactant samples were analyzed using High Performance Liquid Chromatography (HPLC) in conjunction with an ultraviolet light detector and integrator. The surfactants used for this study, all of which have chromophors as shown in Figure 6, are easily detected by an ultraviolet light detector. The HPLC column was 6 inches long and packed with a C-18 reverse phase silica. Various ratios of HPLC grade methanol and distilled/deionized water ranging from 30 to 90 percent were used to elute the surfactants from the column. In general the column pressure was 2000 psi at a flow rate of 3 milliliters per minute. Calibration curves generated from HPLC analysis of surfactant standards were used to determine the surfactant concentration of samples produced by the MEUF apparatus.

MEUF studies composed of a mixture of surfactant and TCE were performed using surfactant feed concentrations of 0.05 M. The 0.05 M concentration was selected so the data generated by the liquid-vapor studies could be directly compared with the MEUF

data. The TCE concentrations in samples generated by the MEUF apparatus were evaluated using a Tekmar<sup>®</sup> 2000 purge and trap in conjunction with a Varian 3000 gas chromatograph (GC) with a 60 meter Supelco Vocol megabor column and a Tracor 1000 Hall Detector. The carrier and purge gas was helium and the reactor gas was hydrogen. The purge-and-trap apparatus was operated in a headspace analysis mode due to the presence of foaming agents (surfactants) in the samples. The headspace analysis was performed by purging for 12 minutes the headspace above 5 milliliters of sample solution thermostatted at 40°C. Two calibration curves were generated since the vapor pressure of TCE is directly related to the presence of micelles. The permeate samples were compared against calibration curves generated by TCE standards with surfactant concentrations below the CMC. Retentate samples were compared against calibration curves generated by TCE standards with surfactant concentrations of 0.05 M surfactant.

## **B. VACUUM STRIPPING**

The stripping of TCE from surfactant solutions was studied at a 0.2 M surfactant concentration. The study was performed at 22°C using a 20-liter glass vessel maintained at 26 inches of mercury by a dry reciprocating pump powered by a one forth horsepower 120 volt motor. The mixture of TCE and surfactant solution was introduced into the glass vacuum chamber by a spray nozzle at a rate of 114 milliliters per minute. After samples were taken from the vacuum stripped solution the solution was recycled into the vacuum vessel for further vacuum stripping. The samples were analyzed using the Tekmar<sup>®</sup> 2000, Varian GC, and Hall detector using the same method as was used for MEUF samples of TCE surfactant mixtures except that the TCE calibration curves were generated using TCE standards in a 0.2 M surfactant solution.

## **C. VAPOR-LIQUID EQUILIBRIUM**

Vapor-liquid equilibrium studies of TCE in aqueous solutions and in 0.05 M surfactant solutions were done by analyzing the vapor in the headspace above the liquid phase using gas chromatography. Samples of twenty milliliters of aqueous solution and surfactant solution with known concentrations of TCE in 40 milliliter-EPA standard water analysis vials were allowed to equilibrate in a temperature controlled bath for 24 hours at one of the following temperatures: 10°C, 20°C or 30°C. After the samples had equilibrated, 0.5 milliliters was drawn from the headspace above the liquid and evaluated using a Perkin-Elmer gas chromatograph. A 3-foot long and 1/8-inch outside diameter column packed with a porous polymer based on 2,6-diphenyl-p-phenylene oxide with a mesh range of 80/100 was used at column temperatures of 180°C, injection temperature of 190, and a detector temperature of 200°C. The carrier gas was helium and the detector gas was hydrogen.



The Dowfax series of surfactants received from the manufacturer contained as much as 2 percent methylene chloride and four percent salts. The salts were removed by diluting the surfactant with distilled/deionized water and ultrafiltering the resultant surfactant solution and discarding the permeate. The process was stopped when the salt peak was reduced by 90 percent as measured by HPLC in conjunction with a conductivity detector. The methylene chloride was removed by boiling a 0.2M surfactant solution at a pressure of 17 inches of mercury for 35 minutes. The temperature of the solution ranged from 80°C to 90°C with the most vigorous boiling occurring at the beginning of the process. This was accomplished in six liter batches which were allowed to cool overnight. Samples of the surfactant solution were evaluated using the Tekmar<sup>®</sup> 2000, Varian GC and Hall detector. No methylene chloride was detected. Dow Chemical Co. now produces DOWFAX 8390 free of methylene chloride.

## SECTION IV

### CONCLUSIONS

The surfactant of choice found in these studies was DOWFAX 8390, a disulfonate with an average molecular weight of 642. This surfactant has a low tendency to precipitate, low leakage through the membrane into the permeate, can be removed from the permeate from the last stage by ultrafiltration with a small pore size membrane, a reasonable flux, and a reasonable solubilization capacity for TCE. Experiments and calculations with this surfactant have shown that approximately four stages would result in a cost efficient pollution control process capable of removing 99+ percent of TCE from water. The envisioned process would only emit pure water and a pure TCE stream. Preliminary economics show that the cost of this process is on the same order as competitive techniques which have undergone substantial development. Moreover, improvements from future research could make the MEUF process superior to alternative technologies.

## **SECTION V**

### **RECOMMENDATIONS**

This feasibility study of MEUF shows enough promise to justify further work to improve its performance. Laboratory work to find a surfactant or surfactant mixture with better flux and solubilization capacity would improve the economics of this process substantially if successful. This process needs to be demonstrated with a pilot unit on a site with TCE contaminated water to really establish its feasibility. Building and operation of such a pilot unit is recommended to demonstrate the promise of MEUF in this application.

## SECTION VI

### REFERENCES

1. The Merck Index, Tenth Edition, Merck & Co., Inc., Rahway, New Jersey, (1983), p. 1378.
2. Leung, P.S., "Surfactant Micelle Enhanced Ultrafiltration," in *Ultrafiltration Membranes and Applications* (A.R. Cooper, Ed.), Plenum, New York (1979) p. 415.
3. Dunn, R.O., Scamehorn, J.F., and Christian, S.D., "Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics from Aqueous Streams," *Sep. Sci. Technol.*, **20**, 257 (1985).
4. Dunn, R.O., Scamehorn, J.F., and Christian, S.D., "Concentration Polarization Effects in the Use of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organic Pollutants from Wastewater," *Sep. Sci. Technol.*, **22**, 763 (1987).
5. Gibbs, L.L., Scamehorn, J.F., and Christian S.D., "Removal of N-Alcohols From Aqueous Streams Using Micellar-Enhanced Ultrafiltration," *J. Membrane Sci.*, **30**, 67 (1987).
6. Smith, G.A., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Equilibrium Solubilization of Benzene in Micellar-Enhanced Ultrafiltration of Aqueous Solutions of Benzene," *Ordered Media in Chemical Separations* (Hinze, W.L., and Armstrong, D.W., Eds.), ACS Symp. Ser., Vol. 342 (1987) p. 184.
7. Bhat, S.N., Smith, G.A., Tucker, E.E., Christian, S.D., Smith, W. and Scamehorn, J.F., "Solubilization of Cresols by N-Hexadecylpyridinium Chloride Micelles and Removal of Cresols From Aqueous Streams by Micellar-Enhanced Ultrafiltration," *Ind. Eng. Chem. Res.*, **26**, 1217 (1987).
8. Scamehorn, J.F., and Harwell, J.H., "Surfactant-Based Treatment of Aqueous Process Streams," in *Surfactants in Chemical/Process Engineering* (Wasan, D.T., Shah, D.O., and Ginn, M.E., Eds.), Marcel Dekker, New York, (1988), P. 77.
9. Scamehorn, J.F., and Harwell, J.H., "An Overview of Surfactant-Based Separation Processes," in *Surfactants in Emerging Technologies* (M.J. Rosen, Ed.), Marcel Decker, New York, 1987, P. 169.
10. Christian, S.D., and Scamehorn, J.F., "Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics from Water," in *Surfactant-Based Separation Processes* (Scamehorn, J.F., and Harwell, J.H., Eds.), Marcel Dekker, New York, 1989, Ch. 1.

11. Harwell, J.H., and Scamehorn, J.F., "Treatment of Hazardous and Toxic Wastes Using Surfactant-Based Separations Processes," in *Management of Hazardous and Toxic Wastes in the Process Industries* (Kolaczowski, S.T., and Crittenden, B.D., Eds.), Elsevier, London, 1987, p 352.
12. Dunn, R.O., Scamehorn, J.F., and Christian, S.D., "The Use Of Micellar-Enhanced Ultrafiltration to Remove Dissolved Organics and Multivalent Transition Metal Cations from Aqueous Streams," *Colloid Surf.*, **35**, 49 (1989).
13. Smith, G.A., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Group Contribution Model for Predicting the Solubilization of Organic Solutes by Micelles," *Langmuir*, **3**, 598 (1987).
14. Schechter R.S., Kandori, K., "Selection of Surfactants for Micellar-Enhanced Ultrafiltration," *Sep. Sci. Tech.*, **25**, 83 (1990).
15. Roberts, B.L., Scamehorn, J.F., Christian, S.D., "Scale-Up of Micellar-Enhanced Ultrafiltration for the Recovery of Dissolved Organics from Aqueous Process Streams," In Preparation.
16. Rosen, M.J., *Surfactants and Interfacial Phenomena*, Wiley, New York, 1978, p. 99.
17. Arshad, S.A., Scamehorn, J.F., and Christian, S.D., "Removal of Chlorobenzene from Water Using Micellar-Enhanced Ultrafiltration," In Preparation.
18. Nguyen, C.M., Christian, S.D., and Scamehorn, J.F., "Measurement of Solubilization Isotherms for Organic Solutes in Aqueous Micellar Solution," *Tenside Surfactant Deterg.*, **25**, 328 (1988).
19. Nguyen, C.M., Scamehorn, J.F., and Christian, S.D., "Solubilization of N-Hexanol in Mixed Micelles," *Colloid Surf.*, **30**, 335 (1988).
20. Smith, G.A., Christian, S.D., Tucker, E.E., and Scamehorn, J.F., "Solubilization of Hydrocarbons by Surfactant Micelles and Mixed Micelles," *J. Colloid Interface Sci.*, **130**, 254 (1989).
21. Counce, R.M., Wilson, J.H., Singh, S.P., Ashworth, R.A., and Elliott, M.G., "Economic Model for Air Stripping of Volatile Organic Chemicals from Groundwater with Emission Controls," *ACS Symp. Ser.*, **468**, 177 (1991).
22. Peters, M.S., and Timmerhaus, K.D., *Plant Design and Economics for Chemical Engineers*. Fourth Edition, Mc Graw-Hill, New York, 1991.